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## Deposition of Polymer Thin Films on ZnO Nanoparticles by a Plasma Treatment

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### ABSTRACT

Ultrathin acrylic acid polymer films have been deposited on the surfaces of nanoparticles of ZnO using a plasma polymerization treatment. The average size of nanoparticles is on the order of 50 nm in irregular shapes. High-resolution transmission electron microscopy (HRTEM) experiments showed that an extremely thin film of the acrylic acid layer (15 nm) was uniformly deposited on the surfaces of the nanoparticles. In particular, the particles of all sizes exhibited equally uniform ultrathin films indicating a well-dispersed nanoparticles in the fluidized bed during the plasma treatment. The deposition mechanisms and the effects of plasma treatment parameters are discussed.

### INTRODUCTION

Nanoparticles are known to have extremely high surface areas. As a result of the high surface area, the surface energy can reach the order of 100 kJ/mol for a variety of materials (1-5). Due to high surface areas, nanoparticles naturally agglomerate and can form considerable bonding between particles. If they strongly bond to each other, they cannot be easily dispersed and are referred to as an aggregate or a hard agglomerate. Therefore, for nanoscale particles, the challenge is that whether they can be well dispersed in space. Furthermore, in a well-dispersed condition, whether it is possible to coat uniformly a thin layer of foreign species on their particle surfaces. In this proposal we will address these issues and focus on the optimization of experimental procedures.

Surface coating of nanoparticles is an important area in nanomaterials synthesis. Because of their special composition, these coatings possess a unique combination of properties of the inorganic and organic components, for instance hydrophobic, hydrophilic, anti-fogging, anti-fouling, anti-adhesive and/or teflon-like properties in combination with hardness and scratch and abrasive resistance. The combination of mutually chemically interconnected organic and inorganic networks results in coatings with a very low permeability for gases and liquids. Hybrid materials are very suitable for application as coatings on a highly diverse spectrum of substrates including glasses, ceramics, plastic, wood, and metal. Before curing, the coating materials consists of a clear alcoholic solution that can easily be processed by classical application techniques such as dipping, spraying, or spin coating. However, in these previous coating processes, the coatings are quite thick up to the order of microns.

The current trend of developing nanophase materials has motivated an increased need for nanometer-scale structures in a variety of applications. Indeed, it is clear that, in order to achieve unique mechanical, physical, chemical, and biomedical properties, it is necessary to develop novel synthesis routes by which an entirely new nanostructure can

be developed. In the past, great efforts have been focused on nanoparticle synthesis, assembly, interfaces, dispersions, and functional devices (1-5). Although high volume (~80 vol.%) polymer coating of nanoparticles has been reported (6), no studies so far have shown uniform deposition of ultrathin films of the order of 10-20 Å on the surface of the nanoparticles, which is, in this letter, referred to as "nanocoating." The deposited film can also be tailored to multi-layers on a nanoparticle. Nanocoating is of particular importance in electronics, functional devices, new materials synthesis, nanobiomolecular applications, tissue engineering, and drug delivery. Using nanocoating, it is possible to alter the intrinsic properties of materials that cannot be achieved by conventional methods and materials.

For nanoscale ceramics particles, the challenge is that whether they can be well dispersed in space. Further, in a well-dispersed condition, it is possible to deposit a thin film of foreign species uniformly on the nanoparticle surfaces and thereby reduce their surface energies. In this study we will address these issues and report experimental data on the deposition of multiple layers of polymer ultrathin films on the surfaces of nanoscale alumina particles by a plasma polymerization process. The deposited thin films are plasma-polymerized pyrrole and hexamethyldisiloxane (HMDSO).

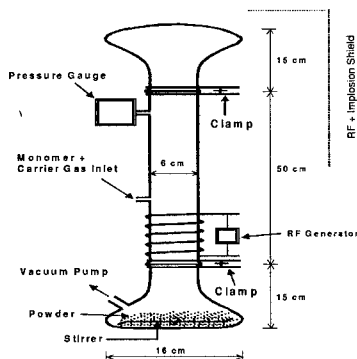
One of the possible applications of nanocoating is in ion exchange for removing metal ions from water. If on the surface of these nanoparticles, an extremely thin layer of polyacrylic film can be coated by a plasma treatment. The polyacrylic film will react with metallic ions in water. As a result of the high surface-to-volume ratio of these nanoparticles, the efficiency of ion exchange in the water flux is much higher than other types of traditional reactors. In this research we have carried out the preliminary experiments in coating nanoparticles with acrylic acid polymer films. The results have shown that, using plasma treatment, a uniform thin film of acid polymer film has been coated on the nanoparticles of ZnO.

## EXPERIMENTAL DETAILS

In this experiment, a RF-plasma reactor was used for the nanoparticle coating. We have selected nanoscale ZnO particles of 50 nm. The schematic diagram of the plasma reactor for thin film deposition of nanoparticles is shown in Figure 1. The vacuum chamber of plasma reactor consists of a long Pyrex glass column about 80 cm in height and 6 cm in internal diameter (7,8).

The nanoparticles of ZnO are vigorously stirred at the bottom of the tube and thus the surface of nanoparticles can be continuously renewed and exposed to the plasma for thin film deposition during the plasma polymerization process. A magnetic bar was used to stir the powders. The gases and monomers were introduced from the gas inlet during the plasma cleaning treatment or plasma polymerization. The system pressure was measured by a pressure gauge. A discharge by RF power of 13.56 MHz was used for the plasma film deposition. Before the plasma treatment, the basic pressure was pumped down to less than 200 mTorr and then the plasma gases or monomer vapors were introduced into the reactor chamber. The operating pressure was adjusted by the gas/monomer mass flow rate. The base pressure was less than 200 mTorr. Acrylic acid (AA) was used as a monomer for plasma polymerization. During the plasma polymerization process, the

input power was 20 W and the system pressure was 450 mTorr. The plasma treatment time was 240 min. Per batch 40 grams of powder were treated.



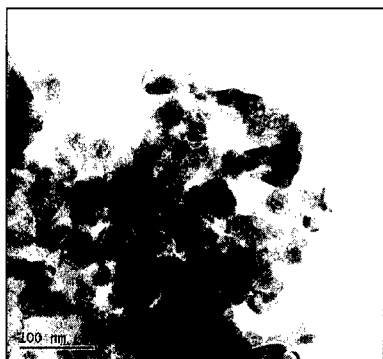
**Figure 1.** Schematic diagram of the plasma reactor for thin polymer film coating of the nano-particles.

After the plasma treatment, the nanoparticles of ZnO were examined by using the high-resolution TEM (HRTEM) experiments performed on a JEM 2010F. In FTIR experiment, potassium bromide (KBr) of 99%+ purity was obtained from Aldrich Chemical Company Inc, Milwaukee, WI. The coated powder was mixed with KBr and pressed into small pellets for the FTIR experiment. FTIR spectra were acquired on a BIO-RAD FTS-40 FTIR spectrometer with a BIO-RAD transmittance attachment.

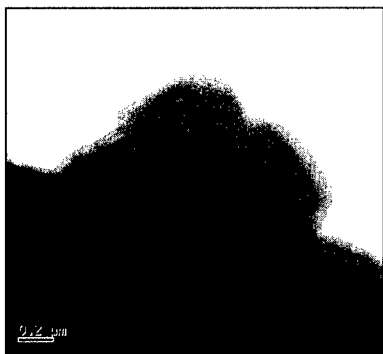
## RESULTS AND DISCUSSION

In transmission electron microscopy, the original and coated ZnO nanoparticles were dispersed onto the holey-carbon film supported by Cu-grids for the TEM operated at 200 kV. Figure 2 shows the transmission electron microscopy (TEM) image of the original, uncoated ZnO nanoparticles. The average particle size is about 50 nm, with the smallest particle size on the order of 15 nm. These particles also exhibit the irregular shapes for all sizes. Figure 3a is the TEM image of the coated particles. Compare to Figure 2, one can see a bright edge on the particle surfaces, which is the result of the polymer coating. Figure 3b is a high magnification image showing a uniform coating on the particle surfaces. In this figure one can see not only that acrylic acid film is uniform but the thickness of the film is also extremely thin on the order of 15 nm.

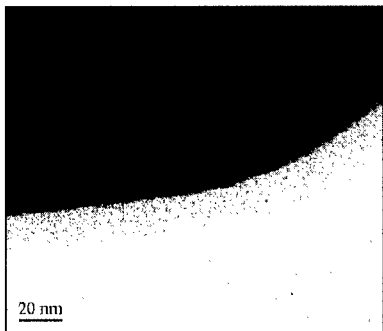
Particularly interesting, although these particles have different diameters, the coating remains the same thickness indicating the uniform distribution of polymer atoms in the plasma chamber. The coating layer is amorphous based on the HREMs of different particles. In contrast, the images of the original particles (Figure 2) do not show the amorphous layer.



**Figure 2** TEM image showing the uncoated ZnO nanoparticles.



**Figure 3a.** TEM images showing acrylic acid coated nano ZnO particles. .

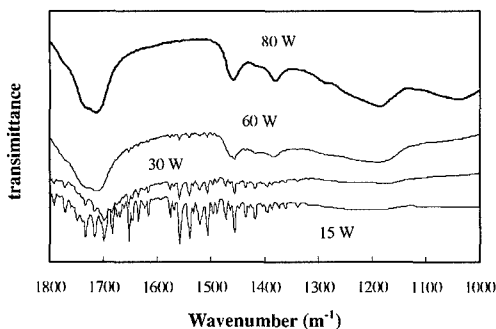


**Figure 3b.** The acrylic acid coating on the surface of ZnO. The film is about 15 nm thick.

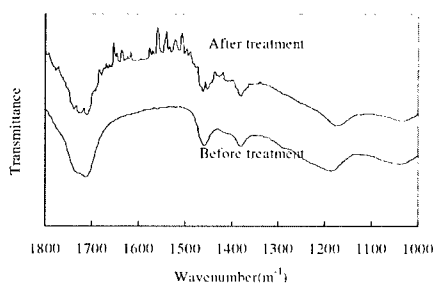
Thus, we are certain that the observed layer is due to coating rather than an artifact in TEM observation.

Figure 4 shows the IR spectra of acrylic acid-coated nanoparticles of ZnO. In this figure, we can see the effect of plasma power on the coating. As the plasma power increases, the peak at about  $1700\text{ mm}^{-1}$  intensifies significantly. This peak at  $1700$  belongs to the function group of C=O vibration. The intensification of this peak indicates an increase of this function group C=O in the deposited films. In ion exchange, more of C=O function groups are needed in order to react with metallic ions in water. In order to investigate the film solubility in water, we immersed acrylic acid-coated nanoparticles in the  $\text{Ni}^{2+}$  solution at room temperature. After 1 hour, the coated nanoparticles were dried and the IR experiment was performed again on these samples. Some of the results at higher power of 60 W are shown in Figure 5. As can be seen, at higher plasma power, the acrylic acid film remains insoluble in water. However, we found that, at lower plasma powers such as 15 W and 30 W, the entire film was removed by the nickel solution indicating there were less cross-links in the polymer. At higher plasma power above 60W, the film becomes insoluble, even the polymer has very strong hydrophilic function groups of "COOH".

During coating, the polymer is introduced as a vapor and the collision frequency increases with the gas pressure. The rate of polymer condensation on the nanoparticle surfaces may be influenced by many parameters such as electron density, temperature, and energy density. Although a systematic study on the optimization of synthesis parameters has not yet been carried out, the preliminary experimental data have indicated that the coating polymer must be stable and not reactive with the substrate during coating. The gas pressure must be moderate for a low collision rate on the nanoparticle surfaces (9,10).



**Figure 4.** IR spectrum of acrylic acid-coated ZnO nanoparticles.



**Figure 5.** IR spectrum of acrylic acid-coated ZnO nanoparticles before and after water test.

In summary, we have deposited an acrylic acid film on ZnO nanoparticles by means of a plasma polymerization treatment. The coating is not only uniform on all particle sizes, but also thin with a thickness of 15 nm. Such coating characteristics are essential in establishing unique nanostructures, tailoring unique physical properties, and pioneering novel synthesis route.

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